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Publication number: **0 217 105 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 27.12.91 (51) Int. Cl.⁵: A61K 7/00, C09K 19/00

(21) Application number: 86111602.8

(22) Date of filing: 21.08.86

(54) Lamella type single phase liquid crystal composition and oil-base cosmetic compositions using the same.

(30) Priority: 02.09.85 JP 193426/85
24.10.85 JP 238165/85

(43) Date of publication of application:
08.04.87 Bulletin 87/15

(45) Publication of the grant of the patent:
27.12.91 Bulletin 91/52

(64) Designated Contracting States:
DE FR GB IT

(56) References cited:
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Description

BACKGROUND OF THE INVENTION

5 i) Field of the Invention

The present invention relates to a novel lamella type, single phase liquid crystal composition and more particularly to such composition as a homogeneous gel, which can be converted into an oily sol of excellent spreadability when water contained therein is evaporated, and is useful as a substrate of cosmetic
10 compositions which are expected to be readily washed off with water.

ii) Description of the Prior Art

Cleansing cosmetics are widely used in order to remove the skin dirt or make-up cosmetics. They are
15 applied to the skin, extended thereon, and finally removed from the skin.

Conventional materials which are commercially available to meet the above purposes are cosmetic compositions containing an oil substance or a water-in-oil type or oil-in-water type emulsion as a substrate. Recently, it has also been reported that a gel of oil-in-surfactant emulsion is applicable as a substrate of cleansing cosmetic compositions (Japanese Patent Application Laid-Open No. 46123/1984).

20 The use of an oil substance or a water-in-oil emulsion in such compositions is accompanied by a disadvantage in that the applied cleansing or massage cosmetics is hardly removed completely because the continuous phase of the cosmetic compositions consists of oil. Ordinary practice, therefore, is to wipe off the waste cosmetics with tissue paper, then completely wash them off with a facial cleanser. However, the use of tissue paper is not favorable in view that it will also remove the horny cells in the skin, and that
25 the oil transferred to the tissue paper gives a sticky feel to fingers. In turn, when an oil-in-water emulsion is used, the waste cosmetics can be washed out without the use of tissue paper but only at an insufficient degree. Especially, the gelled emulsion of oil-in-surfactant type disclosed in Japanese Patent Application Laid-Open No. 46121/1984 has such disadvantages that it gives a sticky feel upon use, and that the storage stability is not good because it is a two phase composition, although it has an excellent emulsion
30 dispersibility and can be readily washed out with water.

Under the above circumstances, development of a substrate for preparing cleansing compositions is still demanded, which can be readily and completely removed with water without use of tissue paper, which will not give a sticky feel on use and will have good storage stability.

35 SUMMARY OF THE INVENTION

The present inventors have made earnest studies for obtaining a substrate which will meet the above requirements and have found that a liquid crystal composition which system lies within the one phase area, prepared from a hydrophilic nonionic surfactant, a water-soluble substance having a hydroxyl group in a
40 molecule thereof, an oil substance, and water is a suitable material for achieving the purpose. The present invention was accomplished based on the above finding.

Accordingly, the present invention provides a lamella type, single phase liquid crystal composition prepared from a hydrophilic nonionic surfactant, a water-soluble substance having a hydroxyl group in a molecule thereof, an oil substance and water, as defined in claim 1. The present invention also provides an
45 oil base cosmetic composition which comprises the liquid crystal composition as a substrate thereof.

DETAILED DESCRIPTION OF THE INVENTION

The hydrophilic nonionic surfactants usable in the present invention are those having an HLB value of
50 10 to 40, selected from polyoxyethylene sorbitan fatty acid esters, oxyethylene derivatives of glycerine fatty acid esters, oxyethylene derivatives of propylene glycol fatty acid esters, polyethylene glycol fatty acid esters, polyoxypropylene alkyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene hydrogenated castor oil and ethylene oxide addition products of Guerbet alcohol having an HLB of 10 to 40. They are used singly or in combination of two or more.
55 Incorporation amount is from 10 to 30 wt% (hereinafter may be referred to simply as %) based on the total weight and preferably from 10 to 20%. Less than 1% will not form a liquid crystal, whereas more than 30% will make the liquid crystal solidified, thus not preferable.

The water-soluble substances having a hydroxyl group in a molecule thereof which are used in this

invention include propylene glycol, 1,3-butanediol, dipropylene glycol, glycerine, diglycerine, polyglycerine, trimethylolpropane, erythritol, pentaerythritol, sorbitan, glucose, sorbitol, mannitol, saccharose, trehalose, polyoxyethylene methyl glucoside, polyoxypropylene methyl glucoside, polyethylene glycol and ethanol. Among them, glycerine, sorbitol and ethanol are especially preferred. They are used singly or in combination. The incorporation amount of the water-soluble substance may vary according to the intended feel on use and viscosity of the final formulation, and may be 5 to 50%, preferably 5 to 15% based on the weight of the total composition.

The above water-soluble substances can be used in combination of two or more. When an ethyleneoxide or propyleneoxide addition product of glucose derivatives is used along with other water-soluble substances, it will mitigate the glow feel or sticky feel, which are causable by the presence of oil, thus the feel on use can be greatly improved. Ethyleneoxide adducts (10 to 30 mol E.O.) of methylglucoside are especially preferred for this purpose. Incorporation amount should be 1.0% or more based on the total weight of the liquid crystal composition for improving the feel on use.

The oil substances usable in this invention are any oils which are ordinarily used in cosmetic compositions. Typical examples are hydrocarbons, esters of a higher alcohol and a higher fatty acid, fatty alcohols, fatty acids, triglycerides, oils or fats of animal and vegetable origin, cholesterol fat, acid esters, among which especially preferred are liquid paraffin, isostearylcholesteryl esters, glyceryl tri-2-ethylhexanoate, octadecyl mirystate and olive oil. These are used singly or in combination. The incorporation amount is from 30 to 80% based on the total weight of the liquid crystal composition.

The amount of water may vary depending upon the use of the final product and the properties intended. Generally, water is present as 1 to 30%, preferably 5 to 30% based on the total composition.

The liquid crystal composition of this invention is prepared by blending a hydrophilic non-ionic surfactant, a water-soluble substance having a hydroxyl group in a molecule thereof, an oil substance and water in such a range that will form a liquid crystal of a single phase. This preparation shows a Bragg space ratio of 1 : 1/2 : 1/3 : 1/4 by the diffraction or low-angle scattering method of X-rays. Also, lamella texture is observed by the polarization microscope. Such a formulation is suitably determined based on the results of blending tests ordinarily carried out by experts skilled in the field. Points to which attention should be paid are the selection of the water-soluble substance, determination of its quantity and the blending ratio. The above parameters should be so determined that will maximize the molecular association of the surfactant when the liquid crystal is under formation.

In order to prepare the liquid crystal composition to be used as a substrate of the cosmetic composition of this invention, a hydrophilic nonionic surfactant, a water-soluble substance having a hydroxyl group in a molecule thereof, an oil substance, and water are blended at a higher temperature than a melting point of respective components to dissolve, then the mixture is cooled down to room temperature as it is stirred. Since a homogeneous liquid crystal is obtained in a single phase, as different from an emulsified composition consisting of two phases of dispersed phase and continuous phase, any order for blending the ingredients will lead to the same liquid crystal composition.

In order to obtain a good cosmetic composition comprising a liquid crystal as a substrate thereof, the liquid crystal can be prepared to have a formulation as follows:

Hydrophilic nonionic surfactant:

Ethyleneoxide addition product of branched fatty alcohol, especially of Guerbet type having from 16 to 24 carbon atoms in total (E.O. addition: 10 to 30 mol)

HLB: 10 to 40

Amount: 10 to 20%

Water-soluble solvent:

Polyol having three or more hydroxyl groups

Amount: 5 to 15%

Oil substance:

Liquid oil, especially ester oil

Amount: 30 to 80%

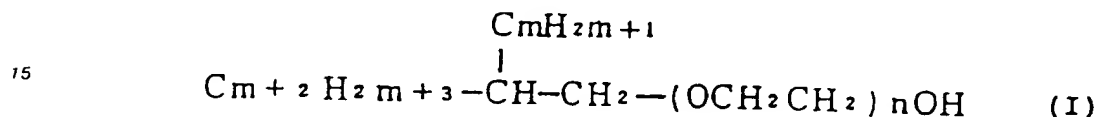
Water:

Amount: 5 to 30%

Ratio of water-soluble substance and water:

5 1:4 to 4:1

Especially preferred liquid crystal composition of this invention is prepared when an ethyleneoxide addition product of Guerbet alcohol having HLB of 10 or more (hereinafter may be referred to as "Guerbet alcohol E.O. adduct") is used for a hydrophilic non-ionic surfactant, and a polyol having three or more hydroxyl groups is used for a water-soluble substance. In this case, example compounds of the usable Guerbet alcohol E.O. adduct are represented by the following formula (I):



wherein m is a number from 6 to 10 and n is a number of 10 to 40.

Among the Guerbet alcohol E.O. adducts of formula (I), especially preferred is such that m is from 7 to 9, and n is from 20 to 30, and may be specifically referred to, for example, polyoxyethylene octyldodecyl ether (25 E.O.), polyoxyethylene heptylundecyl ether (20 E.O.), polyoxyethylene nonyltridecyl ether (30 E.O.).

Examples of the polyol having three or more hydroxyl groups are glycerine, diglycerine, polyglycerine, trimethylolpropane, erythritol, pentaerythritol, sorbitan, glucose, sorbitol, mannitol, saccharose, trehalose, polyoxyethylene methyl glucoside and polyoxypropylene methyl glucoside. Among them, glycerine and sorbitol are especially preferred.

When the lamella type, single phase liquid crystal composition according to the invention is applied to the skin, its chemical structure partially changes as the temperature is elevated because of the skin temperature, HLB value changes owing to water evaporation, and stress is incurred when spreaded on the skin. At this time, the oil substance will serve as a continuous phase and the highly associated hydrophilic nonionic surfactant will serve as a dispersed phase, so that the composition is softened or liquefied. When water is added, thereafter, the hydrophilic nonionic surfactant immediately turns to become a continuous phase, and the oil substance to a dispersed phase. This conversion takes place via a liquid crystal phase. Here, since the hydrophilic nonionic surfactant is oriented extremely densely to the interface between oil and water, the surface tension therebetween is lowered, thereby the oil substance is reduced into extremely small oil-in-water emulsion particles and thus readily removed from the skin surface by water.

Because the liquid crystal composition according to the invention is obtained as a gel, it can be readily handled. Further, when it is applied to the skin, it is softened and then liquefied owing to the skin temperature. This feature is important for obtaining good feeling on use, especially in view of spreadability and smoothness, as well as for obtaining good permeability into the minute portions in the skin. Moreover, when water is added, the oil substance will turn into extremely minute oil-in-water particles, and will be readily removed from the skin. Accordingly, when the liquid crystal composition of this invention is used as a substrate of a cosmetic composition along with ordinary cosmetic ingredients or pharmaceutical agents, excellent cosmetic compositions or drugs for external application can be obtained, which have good storage stability, exhibit non-stickiness on use, have good spreadability and smoothness, and can be readily washed off with water.

The present invention will now be explained by way of examples.

Example 1

Liquid crystal compositions shown in Table 1 were prepared according to the following process, on which the appearance, feel on use, consistency, storage stability and washability were examined. The results are also shown in Table 1.

Preparation

Ingredients (1) to (4) are heated to dissolve at 80°C and mixed. The mixture is cooled down to room temperature while stirred to obtain liquid crystal compositions of the invention.

Table 1

5	Liquid Crystal Composition	Inventive Products		
		1	2	3
10	Composition (%)			
	(1) Polyoxyethylene octyldodecyl ether (20E.O.)	10.0	15.0	20.0
15	(2) Glyceryl tri-2- ethylhexanoate	54.0	51.0	48.0
	(3) Glycerine	25.2	23.8	22.4
20	(4) Purified water	10.8	10.2	9.6
	Ratio (2)/(3)+(4)	1.5	1.5	1.5
25	Characteristics			
	Appearance	translucent flowable gel	transparent gel	transparent gel
30	Feeling on use	non-sticky, refreshing	non-sticky, refreshing	non-sticky, refreshing
35	Consistency (25°C)	a little flowable	good	good
	Storage stability (40°C, 1 month)	good	good	good
40	Washability	good	good	good

45 Example 2

Liquid crystal compositions shown in Table 2 were prepared according to the following process, after which the appearance, feel on use, consistency, storage stability and washability were examined. The results are also shown in Table 2.

50

Preparation

Ingredients (1) to (4) are heated to dissolve at 80°C and mixed. The mixture is cooled down to room temperature while stirred to obtain liquid crystal compositions of the invention.

55

Table 2

Liquid Crystal Composition	Inventive Products				Reference
	4	5	6	7	8
Composition (%)					
(1) Polyoxyethylene octyldodecyl ether (20E.O.)	20.00	20.00	20.00	20.00	20.00
(2) Glyceryl tri-2- ethylhexanoate	73.75	67.50	55.00	52.50	17.50
(3) Glycerine	5.00	10.00	20.00	30.00	50.00
(4) Purified water	1.25	2.50	5.00	7.50	12.50
Ratio of water-soluble substance*	0.8	0.8	0.8	0.8	0.8
Characteristics					
Appearance	transparent gel	→	→	→	transparent flowable gel
Feeling on use	non-sticky, refreshing	→	→	→	→
Consistency (25°C)	a little solid	good	→	→	a little flowable
Storage stability (40°C, 1 month)	good	→	→	→	→
Washability	good	→	→	→	→

$$* : \frac{(3)}{(3) + (4)}$$

Example 3

Liquid crystal compositions shown in Table 3 were prepared according to the following process, after which the appearance, feel on use, consistency, storage stability and washability were examined. The results are also shown in Table 3.

Preparation

Ingredients (1) to (4) are heated to dissolve at 80°C and mixed. The mixture is cooled down to room temperature while stirred to obtain liquid crystal compositions of the invention.

Table 3

Liquid Crystal Composition	Reference	Inventive Products			
	9	10	11	12	
Composition (%)					
(1) Polyoxyethylene octyldodecyl ether (20E.O.)	40	30	20	10	
(2) Glyceryl tri-2- ethylhexanoate	40	50	60	70	
(3) Glycerine	4	8	12	16	
(4) Purified water	16	12	8	4	
Concentration of water-soluble substance*	20	40	60	80	
Characteristics					
Appearance	transparent gel	→	→	→	
Feeling on use	non-sticky, refreshing	→	→	→	
Consistency (25°C)	a little solid	good	→	→	
Storage stability (40°C, 1 month)	good	→	→	→	
Washability	good	→	→	→	

$$* : [(3)/(3)+(4)] \times 100 (\%)$$

Example 4

Compositions shown in Table 4 were prepared according to the following process, after which the appearance, state of the liquid phase, feel on use at the equilibration, consistency, storage stability and washability were examined. The results are also shown in Table 4.

Preparation

For preparing Comparative Product A and the inventive product, the same process described in Example 1 was followed. Namely, ingredients (1) to (4) were heated to dissolve at 80 °C and mixed. The mixture was cooled down to room temperature while stirred to obtain the final compositions.

Comparative Product B was prepared following the process in which ingredient (1) was added into ingredient (3), heated to dissolve and mixed, to which ingredient (2) heated to 80 °C was added and mixed. Emulsion of oil-in-surfactant type was obtained in a gel state. Ingredient (4) heated to 80 °C was further added and cooled down to room temperature while stirred to obtain the final composition.

Comparative Product A did not form a liquid crystal but form an emulsion when the oil phase, aqueous phase, and the surfactant were mixed simultaneously, thus turned out to have unacceptable stability against separation and washability. Comparative Product B, having the same composition as Comparative Product A, was obtained as a gel when the ingredients were blended in a different order. This product exhibited good washability but gave an unfavorable feel on use and separated soon. In contradistinction, the product according to the invention exhibited quite a good washability, good feel on use and long storage stability.

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Table 4

Composition (%)	Comparative Product A	Comparative Product B	Inventive Product
(1) Polyoxyethylene hydrogenated castor oil (50 E.O.)	6	6	20
(2) Liquid paraffin	80	80	60
(3) 1,3-butanediol	7	7	10
(4) Purified water	7	7	10
Preparation	(1)-(4) are heated to dissolve at 80°C and mixed, then cooled down while stirred. Mixture of (3) and (4) heated at 80°C is added with (2) which is heated to dissolve, further added with (1). (1)-(4) are heated to dissolve at 80°C and mixed, then cooled down while stirred.		
State			
Appearance	turbid	gel	gel
Number of phase	2	2	1
Type	crystal	emulsion	Liquid crystal
Characteristics			
Spreadability	not good	not good	good
Stickiness	not good	not good	good
Storage stability (40°C, 1 month)	separated	separated	good
Washability	not good	good	good

Example 5

Liquid crystal compositions shown in Table 5 were prepared according to the following process, after which the appearance, feel on use, consistency, storage stability and washability were examined. The results are also shown in Table 5.

Preparation

Ingredients (1) to (5) are heated to dissolve at 80° C and mixed. The mixture is cooled down to room temperature while stirred to obtain a composition.

Table 5

	Liquid Crystal Composition	Inventive Product	Comparative Product
(1)	Glyceryl tri-2-ethylhexanoate	60	60
(2)	Polyoxyethylene octyldodecyl ether (20E.O.)	15	-
(3)	Polyoxyethylene octadecyl ether (20E.O.)	-	15
(4)	Glycerine	18	18
(5)	Purified water	7	7
Appearance		transparent gel	translucent gel
Feeling on use		non-sticky, refreshing	oily feeling
Consistency (25°C)		good	too flowable
Storage stability (40°C, 1 month)		good	separated
Washability		good	non good

The comparative product containing a linear alcohol E.O. adduct is unhomogeneous because of insufficient gellation, whereas the product according to the invention containing a Guerbet alcohol E.O. adduct is homogeneous and reveals good storage stability. Further, because a phase transition readily takes place, it exhibits good feel on use and good washability.

Example 6

Cleansing Composition

All the following ingredients were heated to dissolve, mixed and then cooled down to prepare a single phase liquid crystal cosmetic composition. (Formulation)

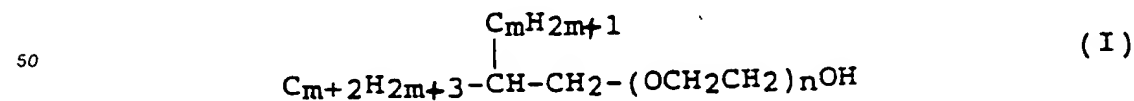
	Sorbitol	10%
5	Polyoxyethylene methyl glucoside (10 E.O.)	5
	Polyoxyethylene octyldodecyl ether (25 E.O.)	15
10	Glyceryl tri-2-ethylhexanoate	60
	Dibutylhydroxytoluene	0.1
15	Methylparaben	0.1
	Butylparaben	0.1
	Perfume	0.1
20	Ethanol	1
25	Purified water	balance

It was liquefied during the cleansing operation, so that the dirt in the minute portions in the skin was dispersed into the composition and readily washed off by water. The dirt removability was very good.

Claims

1. A lamella type, single phase liquid crystal composition for cleansing human skin, comprising:
 - (A) 10 to 30 wt.-% of one or more hydrophilic non-ionic surfactants having an HLB value of 10 to 40 and selected from polyoxyethylene sorbitan fatty acid esters, oxyethylene derivatives of glycerine fatty acid esters, oxyethylene derivatives of propylene glycol fatty acid esters, polyethylene glycol fatty acid esters, polyoxypropylene alkyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene hydrogenated castor oil, and ethylene oxide addition products of Guerbet alcohol,
 - (B) 5 to 50 wt.-% of one or more water-soluble substances having at least one hydroxyl group,
 - (C) 30 to 80 wt.-% of at least one oil substance which is liquid at normal temperature, and
 - (D) 1 to 30 wt.-% of water.

2. A lamella type, single phase liquid crystal composition according to claim 1, wherein said ethylene oxide addition product of Guerbet alcohol is represented by the general formula (I):



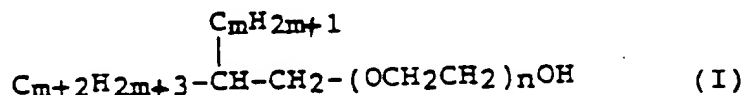
in which m is a number from 6 to 10, and n is a number from 10 to 40.

3. A lamella type, single phase liquid crystal composition according to claim 1, wherein said water-soluble substance is a polyol having three or more hydroxyl groups.

4. An oil base cosmetic composition comprising as a substrate thereof a lamella type, single phase liquid crystal composition as defined in claim 1.
5. A lamella type, single phase liquid crystal composition according to 1, additionally containing an ethyleneoxide or propyleneoxide addition product of a glucose.
6. A method of cleansing human skin which comprises: applying to the skin a lamella type, single phase liquid crystal composition as defined in claim 1 and washing the skin with water to remove said lamella type, single phase liquid crystal composition.

Revendications

1. Composition de cristal liquide à une seule phase, de type feuillet, pour le nettoyage de la peau humaine, comprenant :
 - (A) 10 à 30% en poids d'un ou plusieurs agents tensio-actifs non-ioniques hydrophiles, ayant une valeur HLB de 10 à 40 et choisis parmi les esters d'acides gras et de sorbitan polyoxyéthylénés, les dérivés oxyéthylénés d'esters d'acides gras et de glycérol, les dérivés oxyéthylénés d'esters d'acides gras et de propylène glycol, les esters d'acides gras et de polyéthylène glycol, les alkyl éthers polyoxypropylénés, les alkyl éthers polyoxyéthylénés polyoxypropylénés, les alkyl phényl éthers polyoxyéthylénés, l'huile de ricin hydrogénée polyoxyéthylénée, et les produits d'addition d'oxyde d'éthylène sur l'alcool de Guerbet ;
 - (B) 5 à 50% en poids d'une ou plusieurs substances solubles dans l'eau, ayant au moins un groupe hydroxyle ;
 - (C) 30 à 80% en poids d'au moins une substance huileuse, est liquide à la température ambiante ; et
 - (D) 1 à 30% en poids d'eau.
2. Composition de cristal liquide à une seule phase, de type feuillet, selon la revendication 1, dans laquelle ledit produit d'addition d'oxyde d'éthylène sur l'alcool de Guerbet est représenté par la formule générale (I) :



dans laquelle :

- m est un nombre de 6 à 10 ; et
- n est un nombre de 10 à 40.

3. Composition de cristal liquide à une seule phase, de type feuillet, selon la revendication 1, dans laquelle ladite substance soluble dans l'eau est un polyol ayant trois groupes hydroxyle ou davantage.
4. Composition cosmétique à base d'huile comprenant, en tant que substrat, une composition de cristal liquide à une seule phase, de type feuillet, telle que définie à la revendication 1.
5. Composition de cristal liquide à une seule phase, de type feuillet, selon la revendication 1, contenant en outre un produit d'addition de l'oxyde d'éthylène ou de l'oxyde de propylène sur un glucose.
6. Procédé de nettoyage de la peau humaine qui comprend : l'application sur la peau d'une composition de cristal liquide à une seule phase, de type feuillet, telle que définie à la revendication 1, et le lavage de la peau avec de l'eau pour éliminer ladite composition de cristal liquide à une seule phase, de type feuillet.

Patentansprüche

1. Einphasige Flüssigkristallzusammensetzung vom Lamellentyp zum Reinigen von Humanhaut, umfas-

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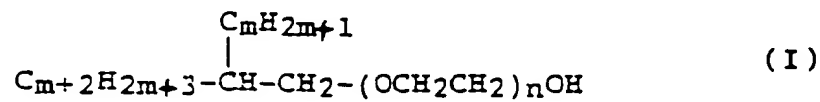
(A) 10 bis 30 Gew.% ein oder mehrere hydrophile nichtionische Surfactantien mit einem HLB Wert von 10 bis 40 und ausgewählt aus Polyoxyethylensorbitan-Fettsäureestern, Oxyethylenderivaten von Glycerinfettsäureestern, Oxyethylenderivaten von Propylenglycolfettsäureestern, Polyethylenglycolfettsäureestern, Polyoxypropylenalkylethern, Polyoxyethylenpolyoxypropylenalkylethern, Polyoxyethylenalkylphenylethern, Polyoxyethylen-hydriertem Rhizinusöl und Ethylenoxidadditionsprodukten von Guerbet-Alkohol.

(B) 5 bis 50 Gew.% ein oder mehrere wasserlösliche Substanzen mit mindestens einer Hydroxylgruppe.

(C) 30 bis 80 Gew.% von mindestens einer Ölsubstanz, welche bei Normaltemperatur flüssig ist, und

(D) 1 bis 30 Gew.% Wasser.

2. Einphasige Flüssigkristallzusammensetzung vom Lamellentyp gemäß Anspruch 1, wobei das Ethylenoxidadditionsprodukt von Guerbet-Alkohol durch die folgende Formel (I) dargestellt wird:



wobei m eine Zahl von 6 bis 10 ist, und n eine Zahl von 10 bis 40 ist.

3. Einphasige Flüssigkristallzusammensetzung vom Lamellentyp gemäß Anspruch 1, wobei die erwähnte wasserlösliche Substanz ein Polyol mit 3 oder mehr Hydroxylgruppe ist.
4. Kosmetische Zusammensetzung auf einer Ölbasis, umfassend als ein Substrat eine einphasige Flüssigkristallzusammensetzung vom Lamellentyp, wie in Anspruch 1 definiert.
5. Eine einphasige Flüssigkristallzusammensetzung vom Lamellentyp gemäß Anspruch 1, die zusätzlich ein Ethylenoxid- oder Propylenoxidadditionsprodukt einer Glukose enthält.
6. Verfahren zum Reinigen von Humanhaut, umfassend die Applikation einer einphasigen Flüssigkristallzusammensetzung vom Lamellentyp, wie in Anspruch 1 definiert, auf die Haut und das Waschen der Haut mit Wasser, um die erwähnte einphasige Flüssigkristallzusammensetzung vom Lamellentyp zu entfernen.

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